Graphitic carbon foams as anodes for sodium-ion batteries in glyme-based electrolytes

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ABSTRACT

The electrochemical performance as potential anodes for sodium-ion batteries of boron-doped and non-doped graphitic carbon foams is investigated by galvanostic cycling *versus* Na/Na$^+$ at different electrical current densities, in glyme-based electrolytes which are known to allow the intercalation of the Na$^+$ ions into graphite. The influence of materials composition and graphitic degree on battery parameters is firstly determined and further discussed by analyzing the mechanism of the electrochemical storage of Na$^+$ ions into these materials which was found to occur through different combinations of pseudocapacitive intercalation and diffusion-controlled intercalation processes. In summary, the results of this study have demonstrated that graphitic carbon foams match a very acceptable capacity with excellent cycle stability as well as performance at high electrical current densities (up to ~ 90 mAh g^{-1} after 300 cycles at 1.9 A g^{-1} with coulombic efficiency ~ 100%) which make them suitable for sodium-ion battery applications. Overall, the increase of the interlayer spacing between the graphene layers and the presence of boron promote the pseudocapacitive intercalation which is responsible for the remarkable rate performance of these materials, whereas the improvement of diffusion-controlled intercalation capacity is mainly related to larger boron content.

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1. Introduction

Sodium-ion batteries (SIBs) were developed alongside lithium-ion batteries (LIBs) in the 1970s and 1980s [1–3], but afterwards they were completely overshadowed by the commercial success of LIBs owing to their higher energy density. However, the natural abundance of sodium (4th most abundant element on earth) as well as its lower cost and environmental awareness as compared with lithium [4], have made SIBs an attractive alternative to LIBs, particularly for large-scale electrical energy storage (EES) systems which are made up of a great number of batteries.

Research on SIBs has grown exponentially since 2010 and it has benefited from the maturity reached after 30 years of R&D on LIBs, specifically in the field of cathodic materials since several of them are drawn up replacing lithium by sodium in the analogue compound such as transition-metal oxides (layered oxides, tunnel oxides) and polyanionic compounds (phosphates, pyrophosphates,

fluorophosphates), with promising results in some instances [5–11]. Likewise, the electrolyte formulations tested for these batteries consist mainly of sodium salts dissolved in organic carbonates mixtures [12,13], some also including ionic liquids (hybrid electrolytes) [14]. In contrast, the development of anodic materials for SIBs has been somewhat more limited, especially regarding carbon-based materials [15–17], since sodium hardly intercalates into graphite - the anode of choice *par excellence* in LIBs - to form binary graphite intercalation compounds (b-GIC). Therefore, only b-GIC of the formula NaC$_{64}$ were obtained in low current density experiments for electrochemical intercalation of Na$^+$ ions in graphite [3], amounting to a reversible capacity of ~35 mAh g^{-1}, which contrasts with the LiC$_6$ intercalation compound attained for Li$^+$ ions (theoretical capacity of 372 mAh g^{-1}). This limitation has been assumed to be the result of the stress induced in the graphite structure by Na$^+$ ions intercalation, and the ionic radius of Na$^+$ ion, which is ~0.3 Å larger than that of Li$^+$ ion [18]. Interestingly, it has been recently circumvented in part by using ether-based electrolytes which allow the electrochemical co-intercalation of solvent molecules along with the Na$^+$ ions to form ternary graphite intercalation compounds (t-GIC) in a highly reversible process. Taking

advantage of this co-intercalation phenomena which was firstly applied to SIBs using a diglyme-based electrolyte by Jache and Adelhem [19], reversible capacities in the range 100–150 mAh g^{-1} with coulombic efficiency and capacity retention approaching 100% as well as excellent rate capability were reported for graphite anodes [20–23]. First of all, these findings have demonstrated that, in contrast to the general belief, graphite is a promising anode material for SIBs. In addition, they are interesting enough to explore the impact on battery performance of different electrolyte solvents able to form t-GIC [22,24] as well as graphitic materials other than stricto sensu graphite that, to the best of our knowledge, have not been studied previously.

Carbon foams (CFs) are lightweight materials with high mechanical strength, high temperature tolerance, low thermal expansion coefficient and tailorable thermal and electrical conductivities which make them suitable for several applications, including active materials for electrodes of energy storage devices, particularly after graphitization by heat treatment at high temperature [25]. Different carbon materials can be used as precursors for the manufacture of graphitic carbon foams (GCFs), such as polymers, mesophase pitches and coals [25]. Among them, coals are an economical alternative because, in addition to availability, the carbon foam production does not require any previous precursor preparation, foaming agents or stabilization steps [26]. Coal-based carbon foams with different properties were prepared by a simple coal carbonization process by adjusting both operating conditions (temperature and pressure) and coal plastic behavior. A subsequent heat treatment at high temperature (≥2400 °C), in an inert atmosphere, was reported to achieve their transformation into graphitic foams with very high degree of three-dimensional structural order, particularly in the presence of boron [27]. Thus, GCFs with crystalline parameter values (d_{002} ~ 0.3365 nm, L_c ~ 41 nm, L_a ~68 nm) and porosity (S_{BET} ~ 4 m^2 g^{-1}) comparable to oil-derived synthetic graphite, which is massively used as anode in commercial LIBs, were prepared. In this context, several boron-doped and non-doped coal-based GCFs were successfully applied as active materials in the anodes of these batteries [28].

With these precedents in mind, the electrochemical performance as potential anodes in SIBs of several boron-doped and non-doped GCFs that were prepared from a bituminous coal [27,28] is herein investigated by galvanostatic cycling at constant and variable electrical current density, using two glyme-based electrolytes, namely sodium triflate (sodium trifluoromethanesulfanate, NaOTf) in diglyme (diethylene glycol dimethyl ether, DG) or in tretraglyme (tretraethylene glycol dimethyl ether, TTG). The results are discussed in terms of battery reversible capacity, irreversible capacity in the first cycle, capacity retention along cycling and cycle efficiency by considering the influence of GCFs composition and graphitic degree as well as of electrolyte solvent properties. The mechanism of interaction of Na$^+$ ions with GCFs is also analyzed through cyclic voltammetry experiments at different sweep rates, following a method which is based on the dependence between peaks currents and scan rates [29]. By this method, the contributions of diffusion-controlled intercalation and capacitive Na$^+$ reactions, which were reported to occur during sodium electrochemical storage in natural graphite [23], to the total sodiation capacity of GCFs electrodes are quantified and related to both composition and graphitic degree.

2. Materials and methods

2.1. Graphitic carbon foams: preparation and structural/textural characterization

A low volatile bituminous coal from USA (Litwak) was selected as the precursor of the carbon foams. Characterization data of the coal is reported elsewhere [27]. Boron oxide (B_2O_3) was used as boron source. The carbon foams (boron-doped and non-doped) were prepared by a two-stage procedure and further heat treated in the temperature interval 2400–2800 °C for 1 h in argon flow, by using a graphite electrical furnace. The experimental set-up can be found in Refs. [27,28]. The graphitized boron-doped carbon foams were identified by the initial boron loading (5B or 10B wt.%), and the treatment temperature (24 for 2400 °C, 26 for 2600 °C, etc.), such as 5B24. Correspondingly, the non-doped graphitized carbon foams were named 0B24, 0B26 or 0B28. Besides these, another non-doped graphitic carbon foam, denoted MCF28, was obtained from one commercial mesophase-based carbon foam by heat treatment at 2800 °C.

Boron contents in the GCFs were determined by inductively coupled plasma (ICP) mass spectrometry. The samples were firstly digested by fusing with sodium peroxide and then dissolved in water together with a small amount of hydrochloric acid. The boron in the solutions was analyzed by standard additions.

The interlayer spacing, d_{002}, and the mean crystallite sizes along a, L_a, and c, L_c, axes are used to evaluate the degree of graphitic structural order of the carbon foams [30]. They were calculated from the X-ray diffractograms which were recorded in a Bruker D8 powder diffractometer as described elsewhere [31]. The d_{002} was determined from the position of the (002) peak by applying Bragg's equation while the L_c and L_a were calculated from (002) and (110) peaks, respectively, using the Scherrer formula, with values of K = 0.9 for L_c and K = 1.84 for L_a [32]. The broadening of diffraction peaks due to instrumental factors was corrected with the use of silicon standard. Typical standard errors of the XRD parameters are <3% and <8% of the reported values for L_c and L_a, respectively; the interlayer spacing values are more precise, with standard errors of <0.03%.

The textural properties of the carbon foams were measured by N$_2$ adsorption-desorption at −196 °C in a Micromeritics ASAP 2420 volumetric adsorption system. Before measurements, the samples were degassed overnight at 200 °C. The specific surface areas (S_{BET}) were calculated by applying the Brunauer−Emmett−Teller (BET) method, taking 0.162 nm^2 for the cross-sectional area of the nitrogen-adsorbed molecule. Total pore volumes (V_t) were determined by the amount of N$_2$ adsorbed at p/p^o = 0.985. Micropore volume (<2 nm) was calculated from the Dubinin-Radushkevich equation [33].

2.2. Electrolytes: preparation and conductivity/viscosity measurements

Two electrolytes consisting in 1 M solutions of sodium triflate (sodium trifluoromethanesulfanate, NaOTf), supplied by Aldrich, in diglyme (diethylene glycol dimethyl ether, DG) or in tretraglyme (tretraethylene glycol dimethyl ether, TTG) were prepared in a glove box under argon atmosphere, with oxygen and water contents below 0.1 ppm, by magnetic stirring. Solvents were also provided by Aldrich (99.5% DG, 99.0% TTG) and used as received.

The ionic conductivity of the glyme-based electrolytes was measured in the glove box using an XS COND70 conductivity portable meter equipped with a VPT80/1 cell. A HAAKE rotational Viscotester VT5 R was used to measure their viscosities. By this procedure, a disk/spindle is submerged in the solution and the force which is necessary to overcome the resistance of the viscosity to the rotation is measured. The viscosity value in mPa s is automatically calculated by the instrument on the basis of the speed and the geometry of the spindle. According to preliminary tests, a R1 spindle was selected and the measurements were carried out at increasing speeds (up to 200 rpm) from which an average viscosity